PATENT SPECIFICATION

NO DRAWINGS

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The inventors of this invention in the sense of being the actual devisers thereof within the meaning of Section 16 of the Patents Act, 1949, are KARL MAIER, HANS BAUMANN, and DIETER LEUCHS, citizens of Germany and residents, respectively, of 60 Bayernstrasse, Ludwigshafen/Rhein, Germany; 8 Mittaschplatz, Ludwigshafen/Rhein, Germany; and 174 Mundenheimerstrasse, Ludwigshafen/Rhein, Germany.

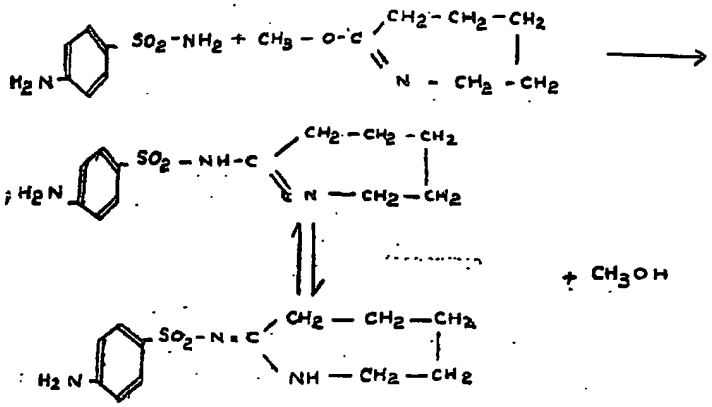
COMPLETE SPECIFICATION

Improvements in the production of Aromatic Aminosulphonyl-Amidines

We, BADISCHE ANILIN- & SODA-FABRIK AKTIENGESELLSCHAFT, a Joint Stock Company organised under the laws of Germany, of Ludwigshafen on Rhine, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

We have found that aromatic aminosulphonylamidines are obtained when an aromatic aminosulphonic acid amide of which the amido and amino groups are unsubstituted is reacted with a lactim-O-alkyl ether, preferably in an indifferent organic solvent, at elevated temperature.

The reaction, for example when using para-aminobenzene sulphonic acid amide and caprolactim-O-methyl ether, is reproduced by the following equation:

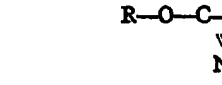


Besides the said aminobenzene sulphonic acid amide, there may also be used as initial materials ring-substituted derivatives of this compound, as for example those which contain alkyl, aryl, aralkyl, cycloalkyl, alkoxy or nitro groups or halogen atoms attached to the ring. There may also be used aromatic aminosulphonamides which have a naphthalene skeleton as the aromatic nucleus. Suitable compounds are for example 1-aminobenzene - 4 - sulphonic acid amide, 1 - aminobenzene - 2 - sulphonic acid amide, 1 - amino-2 - methoxybenzene - 5 - sulphonic acid amide, 1 - amino - 2.5 - dimethoxybenzene-4 - sulphonic acid amide, 1 - amino - 2-methoxy - 5 - methylbenzene 4 - sulphonic acid amide, 1 - amino - 4 - nitrobenzene - 5-sulphonic acid amide, 2 - aminonaphthalene - 6 - sulphonic acid amide, and 1 - amino - 2 - chlorbenzene 5 - sulphonic acid amide.

Among the further reaction components suitable as lactim-O-alkyl ethers there may

[*Price 3s. 6d.*]

be mentioned above all those having the general formula



in which R represents an alkyl group, for example a methyl, ethyl or propyl group, and n a whole number between 3 and 7. The lactim-O-alkyl ethers which come into question are, with the exception of the caprolactim-O-alkyl ethers which are described in the literature (cf. Organic Synthesis, column 31, page 72), new compounds which are readily prepared in an analogous way to the caprolactim-O-alkyl ethers. Suitable lactim-O-alkyl ethers are for example O-methyl-, O-ethyl- and O-propyl-lactim ethers of the lactams as for example alpha-pyrrolidone, alpha-piperidone, caprolactam, oenanthic lactam and caprylic lactam. Derivatives of the lactim-O-alkyl ethers which are substituted in the CH_2-groups by methyl or ethyl radicals, as for example butyrolactim-, valerolactim-, caprolactim-, oenanthic-lactim- and caprylic-lactim-O-alkyl ethers, may also be used.

For the reaction, the reaction components are preferably used in equivalent amounts. In some cases it may be advantageous however to use the lactim-O-alkyl ether in a slight excess, for example 1 to 10% by weight more than is theoretically necessary for the reaction.

The most favourable temperatures for the reaction lie in general between about 40° and 140° C.; it is advantageous to work at about 60° to 100° C.

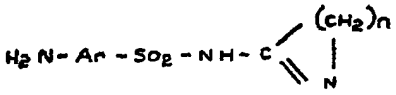
Indifferent solvents, as for example aromatic hydrocarbons, such as benzene, toluene or xylene, aliphatic alcohol, such as methanol, ethanol or propanol, or ethers, for example diethyl ether, or also cyclic ethers, such as tetrahydrofurane and dioxane, may also be co-employed in order to achieve a better thorough mixing of the reaction components. Working in closed vessels may sometimes be necessary, especially when co-employing low-boiling solvents.

The reaction may be carried out for example by mixing the initial materials,, heating the mixture, if desired in the presence of solvents, and keeping it for some at the reaction temperature, for example for 5 to 20 hours. It is also possible however to heat one reaction component, for example the aromatic aminosulphonamide or a solution thereof, to the reaction temperature and to introduce the other component, for example alone or dissolved. Although the reaction already proceeds smoothly under the stated conditions, it may be further accelerated by the addition of catalysts. As substances for accelerating the reaction, which cause a marked effect even in small amounts, for example up to 10% with reference to the lactim-O-alkyl ether, there may be used for example tertiary amines, such as triethylamine, triethanolamine and pyridine.

The aromatic aminosulphonylamidines may be separated from the reaction products by methods known per se, for example by filtration after cooling.

It is already known that cyclic amidines are obtained by allowing an aromatic amine, as for example aniline, to act on caprolactim-O-methyl ether. Aromatic sulphonamides, which contain no further reactive groups on the aromatic ring, have also already been condensed with caprolactim-O-alkyl ethers. It was however unexpected and not to be foreseen that aromatic sulphonamides which contain in addition to the amide group an amino group which is likewise capable of reacting with lactim-O-alkyl ethers, could be smoothly reacted to form the aromatic aminosulphonylamidines.

The aromatic aminosulphonylamidines obtained, which correspond to the general formula

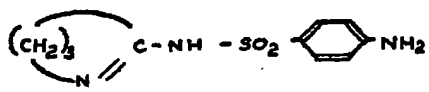


in which Ar represents an aromatic radical and n is a whole number from 3 to 7, are new, valuable compounds. They are pharmacologically active and may also be used for the production of dyestuffs, for example as diazo components, and for the production of pesticides and medicaments.

The following Examples will further illustrate this invention but the invention is not restricted to these Examples. The parts specified in the Examples are parts by weight unless otherwise specified. The parts by weight bear the same relation to parts by volume as the gram does to the cubic centimetre.

EXAMPLE 1.

109 parts of butyrolactim-O-methyl ether and 168 parts of para-aminobenzene sulphonic acid amide in 300 parts by volume of dry xylene are heated to boiling under reflux for 20 hours while stirring. It is then allowed to cool and the deposited reaction product is filtered off by suction. After recrystallisation from water there are obtained 150 parts of the compound of the formula



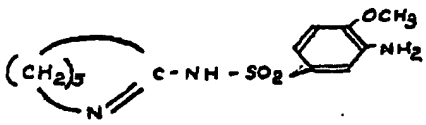
The compound has a melting point of 155° C.

EXAMPLE 2.

40.4 parts of 2-aminoanisol-4-sulphonic acid amide are stirred into 300 parts of methanol and, after the addition of 2 parts of triethylamine and 26.6 parts of caprolactim-O-methyl ether, heated to boiling under reflux for 10 hours while stirring.

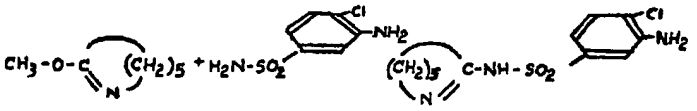
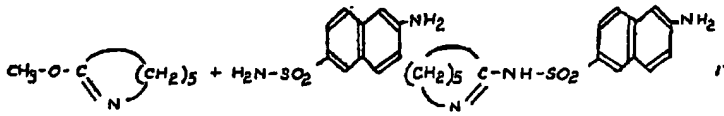
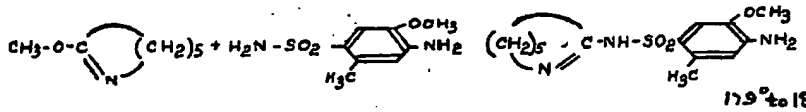
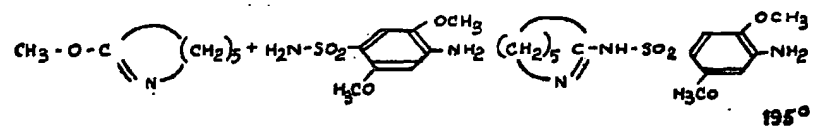
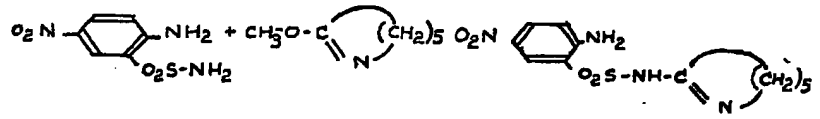
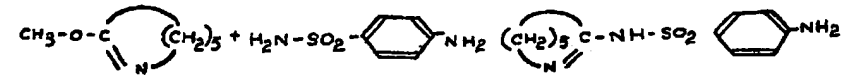
When the reaction is complete, the mixture obtained is cooled and then the deposited solid fraction is filtered off by suction. The filter residue is washed on the filter with ice-cold methanol and dried in vacuo. 50.5 parts of a colourless crystalline substance of the melting point 150° C. are obtained. The compound is soluble in dilute mineral acids.

Elementary analysis of the compound agrees with the formula:



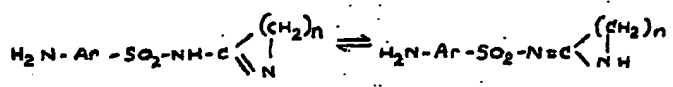
With sodium nitrite it reacts to form a diazo compound of coupling.

In the way above described, the compounds set out in the following table may be obtained in similarly good yields from the initial materials specified in the table:

Initial materials	Product obtained	Melting point
		140° to 141°
		176° to 177°
		179° to 180°
		195°
		130°
		151°
		193°

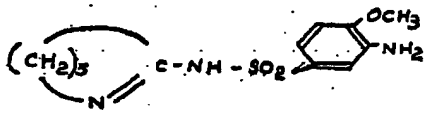
WHAT WE CLAIM IS:—

1. Any aminosulphonylamidine of the general formula

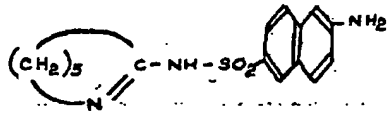


in which Ar represents an aromatic radical and n a whole number from 3 to 7.

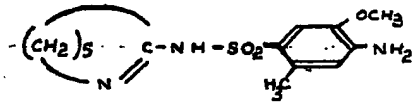
2. The compound of the formula



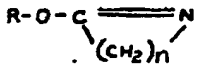
3. The compound of the formula



4. The compound of the formula



5. A process for the production of aromatic aminosulphonylamidines wherein an amino-substituted aromatic sulfonamide of the formula: $H_2N—Ar—SO_2—NH_2$, in which Ar stands for a divalent arylene radical which may contain halogen atoms, alkyl, aralkyl, cycloalkyl, alkoxy or nitro groups, is reacted with a lactim-O-alkyl ether of the formula



in which R is an alkyl radical and n a whole number between 3 and 7, at elevated temperature.

6. A process according to claim 5 wherein the reaction is carried out in an indifferent organic solvent.

7. A process according to claim 5 or 6 wherein the reaction is carried out in the presence of a tertiary amine as catalyst.

8. The process for the production of aromatic aminosulphonylamidines substantially as described in either of the foregoing Examples.

9. Any of the new aromatic amino sulphonylamidines herein described.

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London, W.C.2,
Chartered Patent Agents,

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